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EXCIMER LASER RESEARCH

J. H. Parks

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Semi Annual Report for Period 16 March 1977 to 15 September 1977

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FOREWORD

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This report describes experimental and theoretical investigations of the mercury monohalides. As a class, these molecules show great promise for achieving high power scalable laser action in the visible portion of the spectrum.

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I. INTRODUCTION

During this report period, research was directed towards an initial assessment of the potential for e-beam pumping of mercury monohalide lasers. Specifically, studies were undertaken to probe the molecular formation channels of $HgCl$ in e-beam pumped mixtures of $Xe/Hg/CCl_4$ and $Ar/Xe/Hg/CCl_4$ mixtures. Consistent with this emphasis, additional experiments were begun to provide the quenching rates of the upper laser level by laser gas mixture components. Theoretical calculations of the mercury monohalide radiative lifetimes were completed which provide necessary inputs for quantitative estimates of these quenching rates as well as the molecular kinetics.

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II. E-BEAM PUMPED $HgCl^*$, $HgBr^*$ LASERS

During this research period the emphasis of e-beam experiments was directed towards developing a clearer understanding of the HgX^* formation kinetics and an evaluation of the laser potential. This effort included measurements of fluorescence efficiency, optimization of laser gas mixtures and output coupling, and initial measurements of HgX^* formation rates via replacement reactions involving the xenon halides. To date, pure e-beam pumping of the mercury monohalide lasers $HgCl^{*}$[1] and $HgBr^*$,[2] achieved the results shown in Tables 1 and 2. Since these studies are extending beyond this research period, these results will be discussed collectively in the following semi-annual report. The relevance of these measurements to mercury monohalide e-beam pumped molecular formation kinetics will be reviewed at that time.

(1)   J. H. Parks, Appl. Phys. Lett. 31, 192 (1977).

(2)   J. H. Parks, Appl. Phys. Lett. 31, 297 (1977).

TABLE 1. HgCℓ LASER CHARACTERISTICS

- Wavelength   5576 $\mathring{A}$

- Gas Mixture

    $Ar/Xe/Hg/CCℓ_4 = 84.7\%/11.1\%/2.1\%/1.1\%$

    Ar 3 Amagats

    Cell Temperature $275^{\circ}C$

- E-Beam Energy Deposition   4.8J

- Intrinsic Efficiency

    (50% Coupling)   3.8%

- Peak Power   1.7 MW

- Pulsewidth   100 nsec

TABLE 2. HgBr LASER CHARACTERISTICS

- Wavelength   5018 Å
- Gas Mixture

    Ar/Xe/Hg/HBr = 86. 4%/10. 8%/2. 0%/. 8%

    Ar 3 Amagats

    Cell Temperature 275°C

- E-Beam Energy Deposition   3 J
- Intrinsic Efficiency

    (2. 5% Coupling)   . 5%

- Peak Power   60 kW
- Pulsewidth   100 nsec

III. HEAVY PARTICLE QUENCHING OF HgX*

During this past research period work was performed to design
an experiment to measure the rates at which laser mixture components
quench the excited state of the mercury monohalide lasers. The efficient
extraction of energy from the mercury monohalide lasers will be optimized
by operation at laser flux levels near the saturation flux, ϕ_s. In the
presence of mixtures such as $Xe/Hg/CC\ell_4$, the $HgC\ell^*$ molecules will
be collisionally de-excited or quenched by these components. If only one
of the mixture species, having a density n_Q, dominantly quenches $HgC\ell^*$
at a rate k_Q, the saturation flux in the absence of bottlenecking is given by

$$\phi_s = (h\nu/\sigma_s \tau_1)(1 + \tau_1 k_Q n_Q). \tag{1}$$

Here $h\nu$ is the laser photon energy, σ_s the stimulated emission cross
section, and τ_1 the $HgC\ell^*$ radiative lifetime. In a real case the quench-
ing by each mixture species will have to be taken into account, and this
will probably include both two and three body quenching processes. Thus,
a measurement of the relevant $HgC\ell^*$ quenching kinetics is necessary
for the determination of the saturation flux and efficient laser operation.
A method of determining the relevant quenching processes for the mercury
monohalide system, relies on optical pumping to produce HgX^* in the
presence of the quenching species

In choosing the best mix for a particular laser system various
components are added to perform different functions. In a discharge,

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for example, components are chosen which will produce a desired electron temperature, stabilize the discharge, have large cross sections for forming the desired upper lasing level, have small optical absorption at the lasing frequency, etc. All these components, however, can, in addition to their desired effect, cause the unintentional quenching of the upper laser level. Quenching can be caused by both the heavy particles and the electrons. It is the purpose of this research to measure the effect of the heavy particles on the upper HgX^* laser level. In the following experimental scheme HgX^* will be produced by optical pumping of the mercury dihalide salt (HgX_2) thus eliminating any ambiguity in the interpretation of the results due to the presence of electrons. This should allow for straightforward interpretation of the data.

The work of Wieland[3] indicates that one can obtain emission from the mercury monohalide excited states (HgX^*) by pumping the stable mercury dihalide salts with ultraviolet light. Wieland has shown that the pump wavelength ranges given in Table 3 optimally produce HgX^*. The range is determined by those wavelengths which restrict the photodissocation channel of HgX_2 to that producing the mercury monohalide state $HgX^* (B^2\Sigma_{1/2}^+)$. For the mercury chloride system, Wieland's work indicates that if $HgCl_2$ is optically pumped by 1700 $\overset{\circ}{A}$ radiation, one observes $HgCl^* (B \to X)$ emission. The Xe_2^* excimer is a well known bright fluoresor with peak emission at 1720 $\overset{\circ}{A}$. Thus, if one were to use a xenon lamp to pump $HgCl_2$, one would produce adequate quantities of $HgCl^*$ for these quenching measurements.

(3)   K. Wieland. Zeits. f. Physik 77, 157 (1932).

TABLE 3.   HgX$_2$ ABSORPTION WAVELENGTHS
FOR HgX*(B$^2\Sigma^+_{1/2}$) PRODUCTION

	λ min ($\overset{\circ}{A}$)	λ max ($\overset{\circ}{A}$)
HgCl	1600	1810
HgBr	1700	1950
HgI	1937	2254

In order to pursue this course of investigation we have designed and built a Π shaped quartz gas discharge tube which is filled with ~200 torr xenon gas to produce Xe_2^* emission. This design is based on the work of Huffman et al.[4] A schematic diagram of the discharge tube and associated experimental equipment is shown in Figure 1. The Xe_2^* emission is coupled into the reaction cell which is heated in a double oven configuration. The HgX_2 salt is heated at one temperature (T_1) in a separate side arm which serves to control the HgX_2 vapor pressure. For $HgCl^*$ measurements, a vapor pressure of $HgCl_2$ ~50 microns is adequate $(T_1 \simeq 90^{\circ}C)$. The main body of the reaction cell is kept at a temperature (T_2) which is <u>higher</u> than T_1 and ensures that the windows remain clear. In this configuration, the vapor pressure and $HgCl_2$ density in the cell is accurately known; for example if $T_2 \simeq 200^{\circ}C$, we have $n(HgCl_2) \simeq 10^{15}$ cm^{-3}. A 1/2 m/JA monochrometer and PM1 is used to record the HgX^* spectra through the side of the cell and since the quartz will not pass the Xe_2^* radiation, only the HgX^* emission will be detected. The lamp is pulsed at 300-400 Hz and a boxcar integrator is used to improve signal to noise. The visible Xe discharge fluorescence is monitored (PM2) at one end of the lamp to check the general behavior of the discharge. The observed reproducibility of the $HgCl^*$ emission assures that the Xe_2^* fluorescence is itself quite reproducible. When taking quenching rate data the $HgCl^*$ fluorescence signal is directly monitored by PM3. A filter for Xe_2^* pump radiation is positioned between the discharge lamp and the reaction cell in order to reduce visible Xe background emission. An additional cell can also be placed between the

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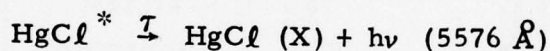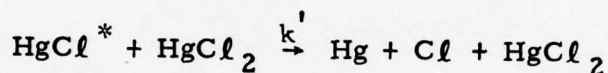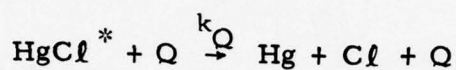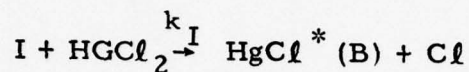(4)   R. E. Huffman et al. Appl. Optics <u>2</u>, 617 (1963).

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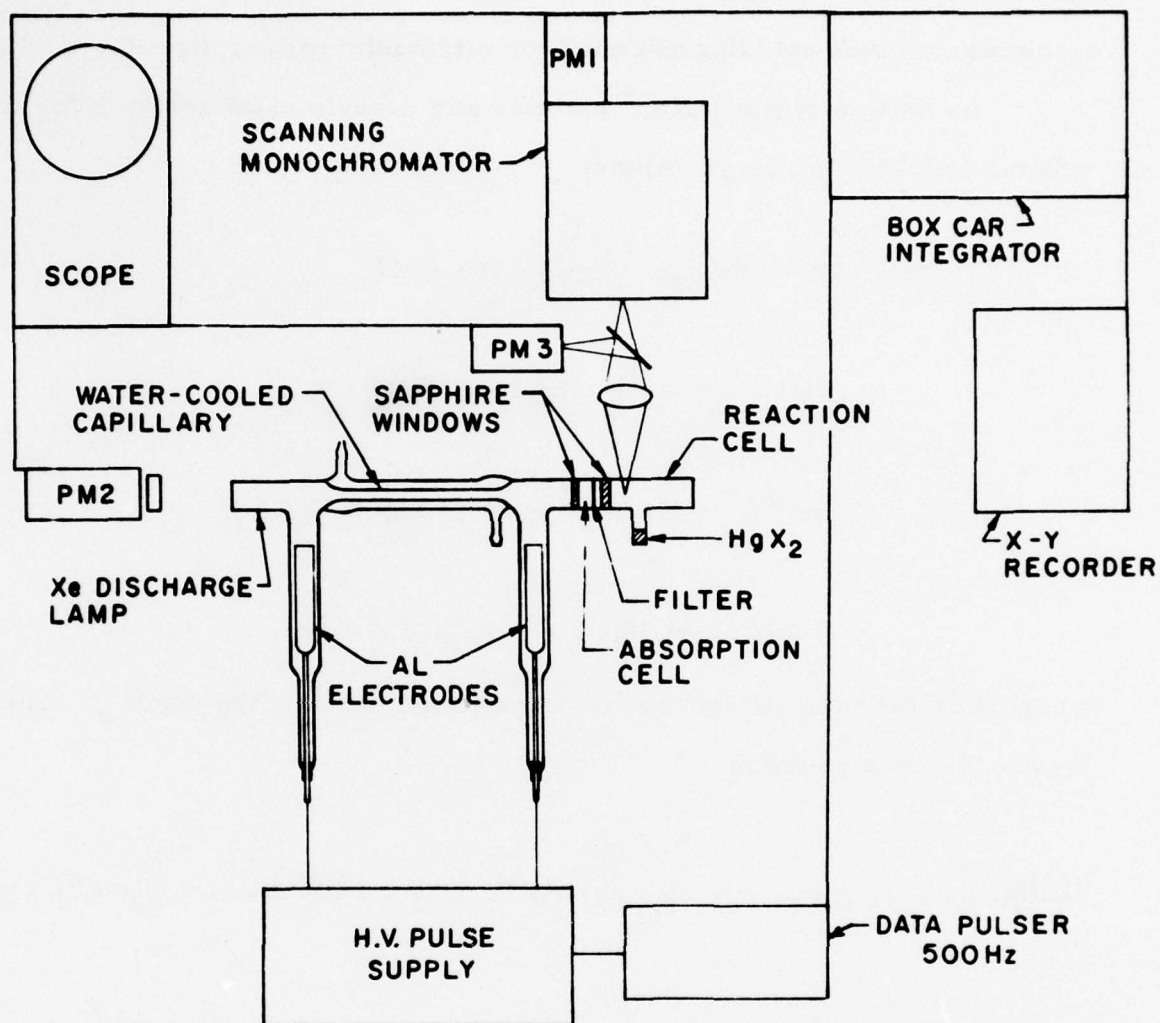
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Figure 1   Schematic of Experimental Apparatus for HgX* Quenching
            Kinetics

lamp and cell to measure the possible ultraviolet absorption by the quenching species. In this case the visible HgX^* emission indicates the ultraviolet transmission thus avoiding the need for ultraviolet measurements.

An outline of the $HgC\ell^*$ kinetics and experimental analysis for this scheme follow from the reactions:

$$I + HGC\ell_2 \xrightarrow{k_I} HgC\ell^*(B) + C\ell$$

$$HgC\ell^* + Q \xrightarrow{k_Q} Hg + C\ell + Q$$

$$HgC\ell^* + HgC\ell_2 \xrightarrow{k'} Hg + C\ell + HgC\ell_2$$

$$HgC\ell^* \xrightarrow{\tau} HgC\ell(X) + h\nu \quad (5576\ \text{Å})$$

where I is the intensity of the Xe_2^* radiation exciting the $HgC\ell_2$. These lead to the rate equation

$$\frac{d[HgC\ell^*]}{dt} = k_I I[HgC\ell_2] - k_Q[HgC\ell^*][Q] - \frac{[HgC\ell^*]}{\tau} - k'[HgC\ell^*][HgC\ell_2]$$

(2)

which has a solution under steady state conditions (i. e., $\dfrac{d[HgC\ell^*]}{dt} = 0$) is given by

$$[HgC\ell^*] = \frac{k_I I[HgC\ell_2]}{k_Q[Q] + 1/\tau + k'[HgC\ell_2]}$$

(3)

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The detected $HgC\ell^*$ emission signal is proportional to

$$S_Q = \frac{[HgC\ell^*]}{\tau} = \frac{k_I \, I[HgC\ell_2]}{1 + k_Q[Q]\tau + k'[HgC\ell_2]\,\tau} \qquad (4)$$

Similarly if $[Q] = 0$, we have

$$S_0 = \frac{k_I \, I[HgC\ell_2]}{1 + k'[HgC\ell_2]\,\tau} \qquad (5)$$

Finally, define the ratio R by

$$R = \frac{S_0}{S_Q} = 1 + \frac{k_Q Q}{1/\tau + k'[HgC\ell_2]} \qquad (6)$$

For expected conditions of the experiment

$$
\begin{aligned}
k_Q &\leq 2 \times 10^{-10} \text{ cm}^3/\text{sec (slightly less than gas kinetic)} \\
\tau\,(HgC\ell^*) &\simeq 3 \times 10^{-8} \text{ sec (Ref. 5)} \qquad\qquad (7)\\
[HgC\ell_2] &\gtrsim 10^{15} \text{ cm}^{-3}
\end{aligned}
$$

we observe that $1/\tau \gg k'[HgC\ell_2]$, i.e. the quenching by the $HgC\ell_2$ background is negligible and R is directly proportional to the quenching rate K_Q

$$R = 1 + k_Q[Q]\tau$$

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(5) N. Djeu and C. Mazza, Chem. Phys. Lett. 46, 172 (1977).

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Thus a Stern-Volmer plot of R vs [Q] yields the slope $k_Q \tau$. Plots of this type will be made for the different mercury monohalides as a function of relevant quenching gases.

During this past research period the apparatus for this experiment was designed and assembled. A preliminary experiment was performed to gain a better understanding of the utility of this technique. In this experiment the $HgCl^*$ (B - X) spectrum was recorded as a function of xenon pressure. The $HgCl^*$ spectrum for a xenon pressure of 200 torr is compared with a spectrum in the absence of xenon in Figure 2. Planimeter measurements show comparable areas (total energy emitted) for these two cases which indicates negligible $HgCl^*$ quenching at this pressure. How-ever, the drastic change in the spectra arises from the rapid relaxation of the $HgCl^*$ vibrational levels by Xe. When [Xe] = 0, the $HgCl^*$ spectrum extends to roughly 3750 Å which is identified with transitions from $B^2\Sigma_{1/2}^+$ levels $v' \sim 20 - 25$ to $X^2\Sigma_{1/2}^+$ levels $v'' \sim 0 - 5$. This $HgCl^*$ photon energy of ~ 3.3 eV corresponds roughly to the Xe_2^* photon energy (6.8 eV) less the $HgCl - Cl$ bond energy of 3.5 eV. This indicates that high vibra-tional levels of the B state are produced in the photodissociation of $HgCl_2$ by Xe_2^* radiation. For [Xe] = 200 torr, the excited state vibrational mani-fold is collisionally <u>relaxed</u> and primarily the strong $v' = 0 \rightarrow v'' = 22 - 15$ radiative transitions are observed. This relaxation can be quite rapid since the vibrational energy spacing is ~ 190 cm$^{-1} \leq$ kT. Comparable results are also observed in $HgCl^*$ laser spectra[1] resulting from mixtures containing a xenon density of ~ 1 amagat.

Preliminary data indicates a two-body xenon quenching rate of $k_{Xe} \sim 3 \times 10^{-13}$ cm^3 sec^{-1}. A most important result indicated by this
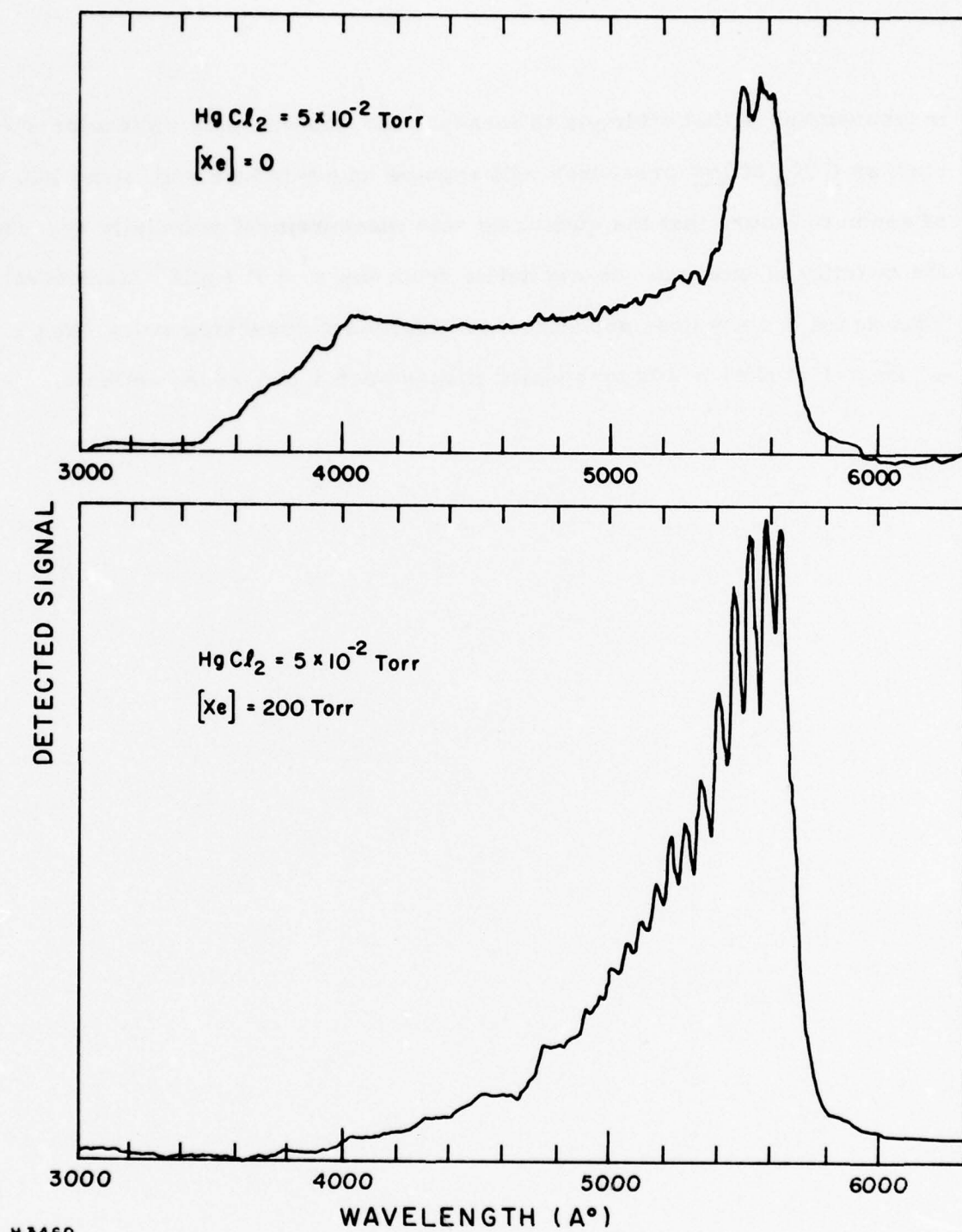
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Figure 2   HgCℓ* (B) Emission for Different Xenon Pressures

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measurement is that attempts to measure the quenching by molecular species such as CCl_4 at <u>low</u> pressures will require an admixture with about 200 torr of xenon to insure that the quenching rate measurement primarily represents the quantity of interest: de-excitation from the $v' = 0$ $HgCl^*$ laser level. This xenon density does not introduce significant quenching since $[Xe] \, k_{Xe} \, \tau \simeq .06 \ll 1$ at $[Xe] = 200$ torr which makes such a procedure reliable.

IV. THEORETICAL EFFORT

This section will discuss the application of a charge transfer model to calculate the oscillator strengths and radiative lifetimes for the mercury-monohalide laser transitions $B^2\Sigma^+_{1/2} - X^2\Sigma^+_{1/2}$. To our knowledge, no previous calculations of the radiative lifetimes of these systems have been attempted. Dunning and Hay[6] have performed _ab initio_ calculations for KrF, in which they computed both the potential energy curves and oscillator strengths.   Their calculation involved an extensive configuration-interaction treatment, utilizing between 2000-3000 configurations.   Although such calculations are valuable, they are enormously time consuming and must be applied individually to each state of each rare gas-halide pair.   This approach is clearly not in a form from which general conclusions can be drawn and applied to the whole class of rare gas-halide systems.   It would therefore be desirable to have available a simpler model, from which one can make fairly reliable predictions for a wide range of systems.   The simple charge transfer theory developed originally by Mulliken[7] and used by Zare and Herschbach[8] for the alkali halides, appears to be a scheme capable of being generalized to a wide variety of systems for which the "ionic-bonding" model holds, including the alkali halides, rare gas-halides, and mercury-monohalides.   The alkali-halide analogy has been extremely

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(6)   P. Hay and T. Dunning Jr., J. Chem. Phys. <u>66,</u> 1306 (1977).

(7)   R.S. Mulliken, J. Chem. Phys. <u>7,</u> (1939) 20.

(8)   R.N. Zare and D.R. Herschbach, J. Mol. Spectry. 15 (1965) 462.

successful[9] in predicting the properties of the rare gas-halides, and the use of the charge transfer model to calculate the transition strengths can be thought of as simply an extension of the analogy.

The basic idea behind the charge transfer theory is that the electron initially localized around the halogen center, in the upper M^+X^- state, "jumps" or is transferred to the mercury positive ion, filling the p-state vacancy, and thus ending up in the MX atomic ground state. This is essentially a "valence bond" picture, in which the electron is transferred from one atomic center to the other. For example, in the mercury chloride $B \rightarrow X$ transition an electron which is initially localized on the Cl atom, forming Cl^-, is transferred to the Hg^+ ion resulting in the ground state configuration of mercury chloride.

In general, the mercury-halides are closely analogous in structure to the rare gas-halides. The upper laser level is "ionic", while the ground state is primarily "atomic". There are, however, some significant differences between the two systems. The upper level of the mercury-halides correlates with the $Hg^+(^2S_{1/2}) + X^-(^1S_0)$ atomic states so that only a single $^2\Sigma_{1/2}$ ionic state is formed. The ground state correlates with the $Hg(^1S_0) + X(^2P_{3/2, 1/2})$ atomic limit, so that we obtain $^2\Pi_{1/2,}$ and $^2\Sigma_{1/2}$ molecular states, as in the case of the rare gas-halides. A more important difference is that the ground states of the mercury-halides are essentially bound states with the binding energy ranging from[10] .36 eV for HgI to 1.8 eV for HgF. With the exception of XeF, which is slightly bound, all of the rare gas-halide ground states are repulsive.

(9)   J. J. Ewing, C. A. Brau, Phys. Rev. $\underline{A12}$, 129 (1975).

(10) G. Herzber, Spectra of Diatomic Molecules, 2nd Ed. (Van Nostrand, Princeton, 1950).

Although the upper and lower states are predominantly ionic and covalent, respectively, it proves to be essential to allow for mixing between these states in order to obtain reasonable results from the theory. The mixed X and B state wavefunctions can be expressed as

$$\Psi_B = N_B \, (\Psi^i + \alpha \, \Psi^c),$$

$$\Psi_X = N_X \, (\Psi^c - \beta \, \Psi^i),$$

(8)

with $\alpha = (\beta - S)/(1 - \beta S)$, and where Ψ^i and Ψ^c are the purely ionic and covalent wavefunctions, N_B and N_X are normalization constants, S is the overlap integral between Ψ^i and Ψ^c, and β is the mixing coefficient. Except for very large values of the internuclear distance, S is non-zero so that S as well as β must appear in the expression for α in order to make the initial and final wavefunctions orthogonal. A major difficulty in the theory is the specification of the mixing parameter β. Given the lack of data on the mercury-monohalides, we have used the procedure outlined by Coulson[11] to estimate the degree of ionic character of the ground state from the electronegativities of the mercury and halogen atoms. The values for the percent ionic character [i. e. $100 \, \beta^2/(1 + \beta^2)$] obtained in this way are given in Table 4. The electronegativities can also be used to determine the co-called covalent-ionic resonance energy, Δ, which is simply the ionic contribution to the binding energy. The values of Δ (in eV) turn out to be 1.2, 0.81, and 0.36 for $HgC\ell$, HgBr, and HgI, respectively, as compared to the experimental dissociation energies (in eV) of 1.0, 0.7, and 0.36. It

(11) C. A. Coulson, Valence, 2nd Ed. (Oxford Univ. Press, London, 1961) pp. 139-141.

TABLE 4. PARAMETERS FOR THE B→X TRANSITION IN THE Hg-HALIDES

	α	β	S	$X^2\Sigma$ Percent Ionic Character	$B^2\Sigma$ Intermuclear Equilibrium Distance(Å)	λ(Å)	μ(Debye)	τ (nsec) Theory	Expt.	Scaled
HgCl	-.64	.53	.87	22	3.15	5576	-6.60	20	--	29
HgBr	-.59	.45	.82	17	3.24	5018	-6.32	16	23[*]	23
HgI	-.51	.35	.73	11	3.50	4412	-5.92	12	--	17

[*]Reference 5

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may thus be inferred that the electronegativity method tends to overestimate the mixing parameter.

In order to complete the definition of the wavefunctions in Eq. 8, it remains to determine the one-electron orbitals that make up Ψ^c and Ψ^i. In keeping with the valence bond picture we have adopted, Ψ^c and Ψ^i are simply taken to be products of unperturbed atomic (ionic) wavefunctions. The analytic Hartree-Fock functions of Cleneti and Roetti[12] were used for the atomic and ionic halogen wavefunctions. Unfortunately, no such functions exist for neutral or singly-ionized mercury. A further complication arises from the fact that relativistic effects are non-negligible for the mercury valence orbital. Since the valence electrons are in an s-state, the most important relativistic effect[13] is a contraction of the radial wavefunction toward the nucleus, due to the absence of a repulsive angular momentum barrier. We have therefore calculated a non-relativistic Hartree-Fock-Slater (HFS) wavefunction, utilizing the Herman-Skillman computer program[14], and scaled the function according to the formula

$$P'(r) = \gamma^{1/2} P_{non-rel.}(\gamma r)$$

so as to reproduce the expectation values $\langle r^n \rangle$ tabulated by Lu et al, [15] from their relativistic HFS program. The calculation was made for $n = -1, 1, 2$ and in all cases $\gamma \approx 1.16$ for Hg; the same value was used for Hg^+. The final function, $P'(r)$, were then represented by a sum of

(12) E. Clementi and C. Roetti, At. Nucl. Data Tables 14 (1974) 177.

(13) V. M. Burke and I. P. Grant, Proc. Phys. Soc. (London) 90 (1967) 297.

(14) F. Herman and S. Skillman, Atomic Structure Calculations (Prentice-Hall, Englewood Cliffs, 1963).

(15) C. C. Lu, T. A. Carlson, F. B. Malik, T. C. Tucker and C. W. Nestor Jr., At. Data 3 (1971) 1.

Slater-type orbitals (STO's) using a nonlinear least squares fitting procedure. The basis set for the 6s functions of Hg and Hg^+ consisted of eight STO's.

With the wavefunctions given in Eq. (8), the transition dipole moment can be reduced to an expression involving only one-electron terms. Consider that the ionic and covalent molecular wavefunctions Ψ^i and Ψ^c are expressed in terms of products of atomic wavefunctions Φ for Hg, Hg^+, X and X^- (X = Cℓ, Br, I) by

$$\Psi^i = (\Phi_{Hg}+)(\Phi_X-)$$

$$\Psi^c = (\Phi_{Hg})(\Phi_X).$$

(9)

These atomic wavefunctions Φ are represented by Hartree-Fock functions composed of products of one-electron wavefunctions, ϕ. Then, the transition dipole moment μ can be shown to be given by

$$\mu = N_B N_X [(\phi_{Hg}|r|\phi_X-\rangle (1 - \alpha\beta)\chi$$

$$+ \alpha\langle\phi_{Hg}|r|\phi_{Hg}\rangle - \beta\langle\phi_X-|r|\phi_X-\rangle],$$

(10)

where ϕ_X- is the initial wavefunction of the active electron centered on the negative halogen ion (X^-), ϕ_{Hg} is the final state one-electron wavefunction, r is the position vector, and χ is an overlap integral involving all of the electron orbitals not involved in the transition. All two-center integrals were evaluated from an expansion developed by Sharma[16] for

(16)   R. R. Sharma, Phys. Rev. A13 (1976) 517.

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the case of one-electron wavefunctions expressed as a sum of STO's. The calculation of the overlap function $S \equiv \langle \Psi^i | \Psi^c \rangle$ and the parameter α for various mercury monohalides are given in Table 4. All these calculations depend on a choice of molecular internuclear separation. An experimental value for the equilibrium internuclear distance exists[17] for the ionic state of $HgC\ell$, but not for the other halides. In order to estimate these distances, the relative sizes of the alkali halides were used as a guide. It was found that the internuclear separation of the alkali bromides are $\approx 3\%$ larger than those of the alkali chlorides while the iodides are $\approx 12\%$ larger. The internuclear distances of the Hg-halides were scaled accordingly, and are given in Table 4.

The results of the calculations f or the $B \rightarrow X$ transitions are summarized in Table 4. The radiative lifetime of the transition is given, in terms of the quantity μ, by $\tau = 3h\lambda^3/64\pi^4\mu^2$ where λ is the transition wavelength. The model predicts a decrease in lifetime with increasing halogen size due to the λ^3-dependence. There is a competing trend caused by a decrease in the dipole matrix element, but this effect is much weaker. In Table 4 we give the experimental result of Djeu and Mazza.[5] The theoretical value is $\approx 30\%$ lower than the measured lifetime, which is quite satisfactory considering the simplicity of the model. Further calculations were carried out to test the sensitivity of the results to the various parameters. When the internuclear distance was varied by 5%, the lifetime changed by less than 5% in all cases. As discussed earlier, the mixing coefficients are the parameters which contain the greatest uncertainty. To give some idea of the sensitivity of our calculation to the percent ionic

(17) K. Wieland, Helv. Phys. Acta 14 (1941) 420.

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character of the ground state, the radiative lifetime of each mercury monohalide is plotted as a function of the mixing coefficient in Figure 3. The value of the mixing coefficient inferred from the electronegativity is indicated for each molecule in Figure 3 by the cross. From our earlier arguments, we expect these mixing coefficients in Table 4 to be over-estimates, so that from Figure 3 the calculated lifetimes are expected to be somewhat too small. This is consistent with the comparison between theory and experiment for HgBr. The sensitivity of the radiative lifetime to a variation of the mixing coefficient β can be estimated from Figure 3. It is easily shown that the variation of a ratio of lifetimes is less sensitive to β and thus a scaling of the calculated lifetimes to the HgBr experimental value is a useful estimate. These scaled lifetimes are also shown in Table 4. Finally, an estimate of the importance of effects such as HgX^* polarization and the broadband emission spectrum were considered and are included in Ref. 18.

(18) C. Duzy, H. A. Hyman, Chem. Phys. Lett. 52, 345 (1977).
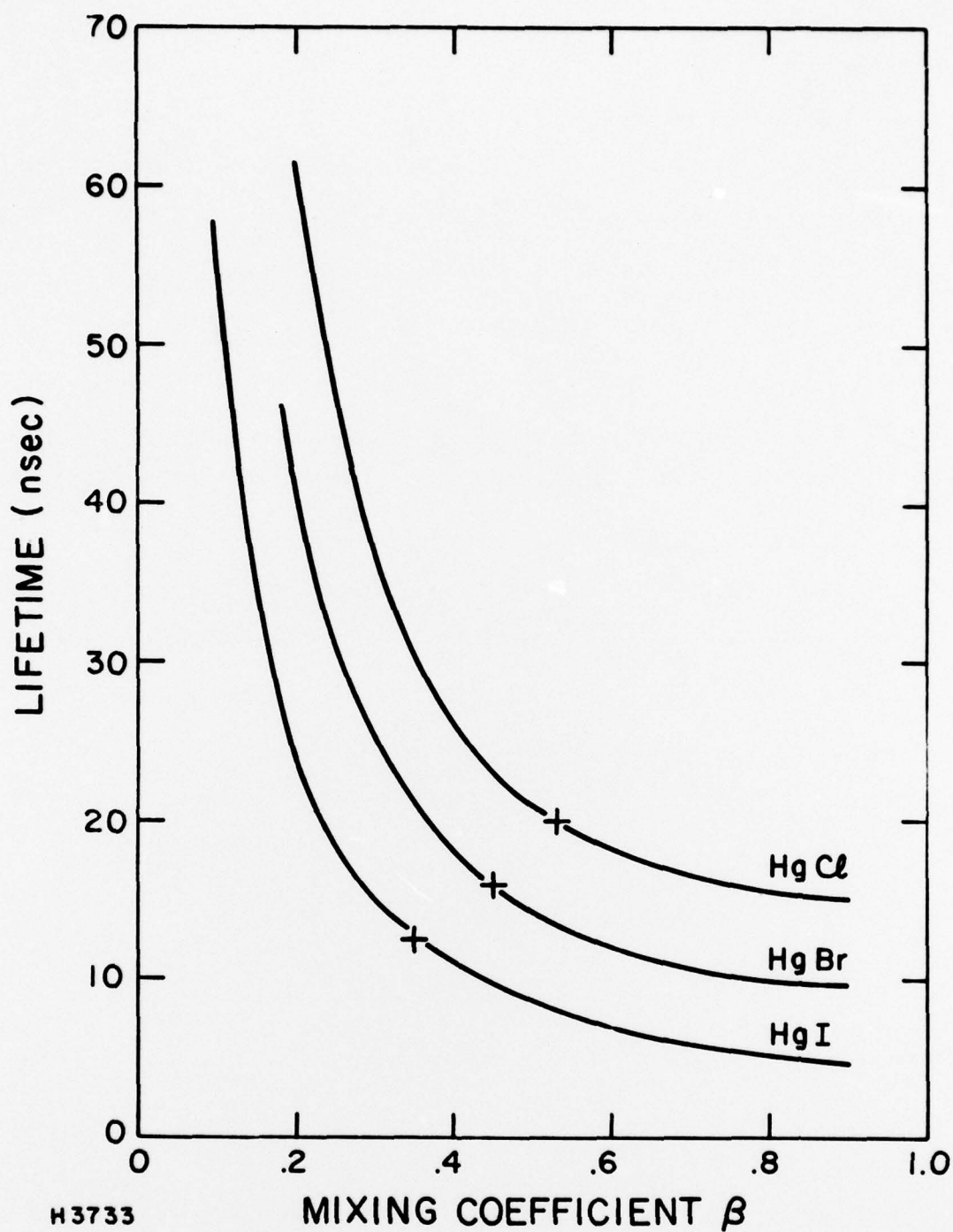
Figure 3   B → X Radiative Lifetime of HgX* as a Function of the Ionic Mixing Coefficient, β

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